

Fig. 3. Packing diagram of the molecules down the *a* axis with intermolecular short contacts (Å).

(without a bridge) is in the chair form. In the cyclohexane ring having the chair conformation, the distance between the planes containing alternate atoms is about 0.433 Å. In the cyclohexane ring having the boat conformation, the atoms forming the 'bottom' of the boat are not exactly coplanar. The deviations of C18 from the planes passing through C16, C15, C19 in molecule *A* and in molecule *B* are 0.296 (6) and 0.286 (5) Å, respectively.

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In molecule *A*, Br1 and O9 are on the opposite sides of the benzene plane, the distances of Br1, O9, O10 from this plane being -0.106 (1), 0.124 (7) and -0.354 (7) Å, respectively. In molecule *B*, however, Br1 and O9 are on the same side of the benzene plane, the distances of Br1, O9, O10 from this plane being -0.035 (2), -0.053 (8) and 0.173 (7) Å, respectively. The dihedral angle between the benzene plane and the plane of the (C8, O9, O10) group is 12.8 (10)° in molecule *A* and 5.9 (10)° in molecule *B*.

Many intramolecular short contacts are present but the intermolecular forces are apparently small [shortest contact C...O, 3.43 (2) Å]. This implies that the molecules are somewhat loosely bound to each other. It is therefore not surprising that the melting point of the compound is rather low (observed m.p. 395 K).

References

- JENNER, P. M., HAGAN, E. C., TAYLOR, J. M., COOK, E. L. & FITZHUGH, O. G. (1964). *Food Cosmet. Toxicol.* **2**, 327–329.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MARUZZELLA, C. J. & BALKER, J. (1959). *Plant Dis. Rep.* **43**, 1143–1145.
 MARUZZELLA, C. J. & BRAMNICK, E. (1961). *Soap Perfum. Cosmet.* **34**, 743–744.
 RAY, S. (1986). *Studies on Natural Products*. PhD Thesis, pp. 192–194. Jadavpur Univ., India.
 ROHMER, M., SCHWARTZ, A. C. & ANTON, R. (1977). *Phytochemistry*, **16**, 773–774.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Structure of 17-Epinimbocinol

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Abstract. 7 α -Hydroxy-4,4,8-trimethyl-21,23-epoxy-24-nor-5 α ,13 α ,17 β -chola-1,14,20,22-tetraene-3,16-

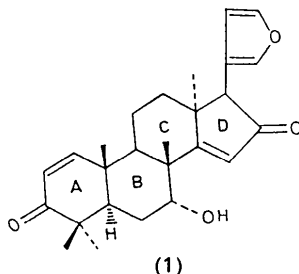
dione, C₂₆H₃₂O₄, *M_r* = 408.51, m.p. = 526–528 K, orthorhombic, *P*2₁2₁2₁, *a* = 6.7094 (9), *b* = 13.195 (1), *c* = 24.281 (3) Å, *V* = 2149.64 Å³, *Z* = 4, *D_x* = 1.262 Mg m⁻³, λ (Cu *K* α) = 1.5418 Å, μ =

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0.584 mm⁻¹, $F(000) = 880$, $T = 291$ K, final $R = 0.0361$, $wR = 0.0449$ for 1820 observed reflections. The *A*–*B* and *B*–*C* rings are *trans* fused. The C(17) furan ring is *trans* to the C(13) methyl and is in the β -position. Intermolecular O—H \cdots O and C—H \cdots O interactions are present.

Introduction. *Azadirachta indica* Juss (syn. *Melia azadirachta*; L. *Melia indica* Margosa), commonly known as neem or nimba, belongs to the family *Meliaceae* and is widely distributed in tropical parts of the world. This plant is well known for its pesticidal activity (Schmutterer, Ascher & Rembold, 1980; Schmutterer & Ascher, 1983) and various other important medicinal properties (Siddiqui, Siddiqui, Faizi & Mahmood, 1988). The nimbidin fraction of the neem oil was found to exhibit antiarthritic, anti-inflammatory (Pillai & Santhakumari, 1981) and antiulcer properties (Pillai & Santhakumari, 1984). The crystal structure of the title compound was studied by X-ray diffraction methods in order to determine the relative stereochemistry.

Experimental. The title tetranortriterpene alcohol (1) was isolated from the nimbidin fraction of the methanol extract of industrial grade neem oil by hydrolysis in a Parr pressure reactor, followed by removing the fatty acids by vacuum distillation and purifying over silica gel with benzene–ethyl acetate (Gaikwad, Mayelvaganan, Vyas & Bhat, 1990). The compound was crystallized from methanol, under ambient conditions, as colourless needles.



A crystal of dimensions 0.4 × 0.5 × 0.4 mm was selected for intensity data collection on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation. Unit-cell parameters were refined from 25 reflections in the range $19 \leq \theta \leq 38^\circ$. Three standard reflections (147, 358, 235), measured every 3600 s, showed no significant intensity variation. Using the ω – 2θ scan technique, a total of 1881 unique reflections were measured in the range $2 \leq \theta \leq 60^\circ$, $h_{\max} = 7$, $k_{\max} = 14$ and $l_{\max} = 27$. Data were corrected for Lp factors and absorption was neglected. The structure was solved by direct methods using *MULTAN*84 (Main, Germain & Woolfson, 1984). Non-H atoms were refined with anisotropic thermal parameters. All H

atoms were located from a difference map and refined isotropically. The structure refinement was by full-matrix least squares based on F values. In the final refinement, 399 parameters were refined using 1820 observed reflections with $|F_o| \geq 3\sigma|F_o|$. Final $R = 0.0361$ and $wR = 0.0449$ {where $w = 1.000/[\sigma(F) + 0.00157F^2]$ }. In the final difference map, $(\Delta\rho)_{\max} = 0.156$ and $(\Delta\rho)_{\min} = -0.138$ e Å⁻³, $(\Delta/\sigma)_{\max} = 0.062$. *SHELX76* (Sheldrick, 1976) was used for the structure refinement and a CYBER 180/840 for computations. Atomic scattering factors were those of *SHELX76*.

Discussion. The atomic coordinates are listed in Table 1, and bond lengths and bond angles are in Table 2.* Fig. 1 is a *PLUTO* (Motherwell & Clegg, 1978) diagram of the molecule. The cyclohexane rings *A*–*B* and *B*–*C* are fused in the *trans* fashion, with torsion angles about H(5)—C(5)—C(10)—C(22) and H(9)—C(9)—C(8)—C(23) of 178.7(4) and 177.6(4)° respectively. Ring *B* has a chair conformation; C(5) and C(8) are 0.743(2) and –0.620(2) Å respectively out of the mean plane formed by the other four ring atoms [maximum deviation ± 0.003 (2) Å]. Ring *C* exists almost in a half-chair conformation with C(9) and C(13) deviating from the least-squares plane passing through the remaining four atoms by 0.710(2) and –0.541(4) Å. The other six-membered ring, *A*, is a twisted boat shape [C(4) and C(10) are –0.384(3) and –0.465(3) Å respectively out of the mean plane passing through C(1), C(2), C(3) and C(5) within a maximum deviation of 0.099(3) Å]. In the case of 7-acetylneotrichilenone (Kraus, Cramer & Sawitzki, 1981), extracted from same plant, all these three rings are in a chair conformation. The five-membered ring has an envelope shape with C(16) –0.215(2) Å out of the plane passing through the remaining four atoms [maximum deviation of ± 0.09 (2) Å]. The furan ring attached to C(17) is planar and *trans* to the C(13) methyl atom [C(18)—C(17)—C(13)—C(24), 141.3°]; in 7-acetylneotrichilenone it is *cis* (Kraus, Cramer & Sawitzki, 1981). The furan ring is in the β -position. The methyl C(22) and C(23) atoms are β , whereas C(24) and O(2) are in an α -orientation (Table 2). The C—C bond distances to the methyl C atom are close to normal values [mean 1.541(4) Å]. However, in cyclopentane rings the C(*sp*³)—C(*sp*³) bond distances range from 1.434(4) to 1.569(3) Å with an average value of 1.527(4) Å, indicative of strain in the molecule. The bond dis-

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53655 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ($\times 10^4$) and equivalent temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	4165 (4)	-3842 (2)	760 (1)	78 (2)
O(2)	4566 (3)	96 (2)	1992 (1)	47 (2)
O(3)	3456 (5)	4004 (1)	2085 (1)	80 (3)
O(4)	-1224 (5)	4958 (2)	617 (1)	89 (3)
C(1)	1654 (4)	-1543 (2)	492 (1)	49 (2)
C(2)	2615 (5)	-2403 (2)	418 (1)	59 (3)
C(3)	3256 (4)	-3071 (2)	868 (1)	51 (2)
C(4)	2672 (4)	-2796 (2)	1455 (1)	45 (2)
C(5)	2437 (3)	-1623 (2)	1484 (1)	38 (2)
C(6)	1993 (4)	-1192 (2)	2053 (1)	42 (2)
C(7)	2488 (4)	-60 (2)	2077 (1)	39 (2)
C(8)	1361 (3)	552 (2)	1635 (1)	35 (2)
C(9)	1579 (3)	36 (2)	1061 (1)	37 (2)
C(10)	1063 (4)	-1123 (2)	1046 (1)	41 (2)
C(11)	597 (5)	662 (2)	603 (1)	53 (3)
C(12)	937 (6)	1803 (2)	639 (1)	61 (3)
C(13)	2575 (4)	2123 (2)	1042 (1)	45 (2)
C(14)	2164 (3)	1621 (2)	1597 (1)	37 (2)
C(15)	2468 (4)	2268 (2)	2015 (1)	49 (2)
C(16)	2952 (4)	3263 (2)	1819 (1)	52 (2)
C(17)	2615 (4)	3275 (2)	1194 (1)	49 (2)
C(18)	792 (4)	3873 (2)	1055 (1)	51 (2)
C(19)	619 (6)	4524 (2)	628 (1)	71 (3)
C(20)	-2237 (6)	4561 (2)	1050 (2)	87 (4)
C(21)	-1090 (5)	3905 (2)	1329 (2)	66 (3)
C(22)	-1185 (4)	-1347 (2)	1112 (1)	54 (2)
C(23)	-846 (4)	658 (2)	1821 (1)	49 (2)
C(24)	4673 (5)	1840 (3)	832 (2)	67 (3)
C(25)	764 (5)	-3395 (2)	1593 (1)	57 (3)
C(26)	4340 (5)	-3138 (2)	1838 (1)	64 (3)

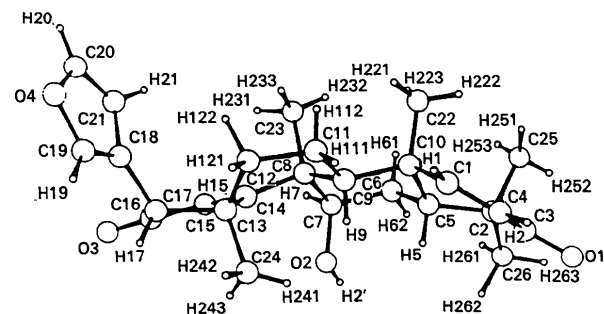


Fig. 1. Perspective view of the molecule.

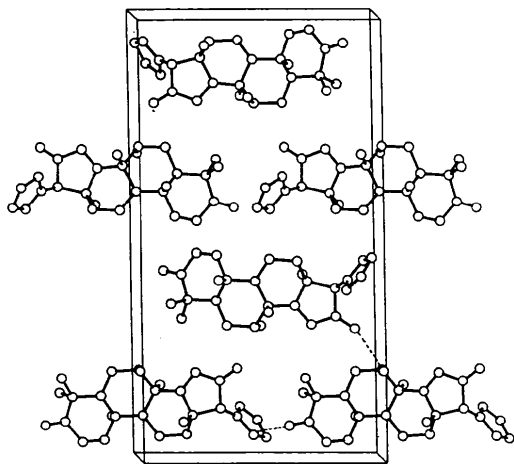


Fig. 2. Unit-cell packing diagram.

Table 2. Bond lengths (\AA), bond angles ($^\circ$), torsion angles ($^\circ$) and hydrogen-bond geometry (\AA , $^\circ$) with e.s.d.'s in parentheses

C(3)—O(1)	1.215 (3)	C(14)—C(8)	1.512 (3)
C(7)—O(2)	1.425 (3)	C(23)—C(8)	1.555 (3)
C(16)—O(3)	1.218 (3)	C(10)—C(9)	1.569 (3)
C(19)—O(4)	1.363 (5)	C(11)—C(9)	1.533 (3)
C(20)—O(4)	1.358 (6)	C(22)—C(10)	1.545 (3)
C(2)—C(1)	1.317 (4)	C(12)—C(11)	1.525 (4)
C(10)—C(1)	1.507 (3)	C(13)—C(12)	1.532 (4)
C(3)—C(2)	1.468 (4)	C(14)—C(13)	1.527 (3)
C(4)—C(3)	1.522 (3)	C(17)—C(13)	1.564 (3)
C(5)—C(4)	1.558 (3)	C(24)—C(13)	1.543 (4)
C(25)—C(4)	1.542 (4)	C(15)—C(14)	1.342 (3)
C(26)—C(4)	1.524 (4)	C(16)—C(15)	1.434 (4)
C(6)—C(5)	1.522 (3)	C(17)—C(16)	1.536 (3)
C(10)—C(5)	1.555 (3)	C(18)—C(17)	1.494 (4)
C(7)—C(6)	1.531 (3)	C(19)—C(18)	1.350 (4)
C(8)—C(7)	1.542 (3)	C(21)—C(18)	1.428 (5)
C(9)—C(8)	1.558 (3)	C(21)—C(20)	1.341 (5)
C(20)—O(4)—C(19)	106.0 (2)	C(9)—C(10)—C(1)	108.7 (2)
C(10)—C(1)—C(2)	124.6 (2)	C(9)—C(10)—C(5)	105.5 (2)
C(3)—C(2)—C(1)	124.0 (2)	C(22)—C(10)—C(1)	106.2 (2)
C(2)—C(3)—O(1)	119.4 (2)	C(22)—C(10)—C(5)	115.2 (2)
C(4)—C(3)—O(1)	122.0 (2)	C(22)—C(10)—C(9)	113.5 (2)
C(4)—C(3)—C(2)	118.6 (2)	C(12)—C(11)—C(9)	115.3 (2)
C(5)—C(4)—C(3)	107.8 (2)	C(13)—C(12)—C(11)	114.6 (2)
C(25)—C(4)—C(3)	107.2 (2)	C(14)—C(13)—C(12)	108.4 (2)
C(25)—C(4)—C(5)	114.5 (2)	C(17)—C(13)—C(12)	115.5 (2)
C(26)—C(4)—C(3)	108.2 (2)	C(17)—C(13)—C(14)	102.6 (2)
C(26)—C(4)—C(5)	109.9 (2)	C(24)—C(13)—C(12)	112.1 (3)
C(26)—C(4)—C(25)	109.0 (2)	C(24)—C(13)—C(14)	110.6 (2)
C(6)—C(5)—C(4)	115.6 (2)	C(24)—C(13)—C(17)	107.3 (2)
C(10)—C(5)—C(4)	116.8 (2)	C(13)—C(14)—C(8)	121.5 (2)
C(10)—C(5)—C(6)	110.3 (2)	C(15)—C(14)—C(8)	127.0 (2)
C(7)—C(6)—C(5)	110.9 (2)	C(15)—C(14)—C(13)	111.3 (2)
C(6)—C(7)—O(2)	110.3 (2)	C(16)—C(15)—C(14)	111.5 (2)
C(8)—C(7)—O(2)	107.7 (2)	C(15)—C(16)—O(3)	128.4 (3)
C(8)—C(7)—C(6)	112.3 (2)	C(17)—C(16)—O(3)	123.8 (3)
C(9)—C(8)—C(7)	110.3 (2)	C(17)—C(16)—C(15)	107.7 (2)
C(14)—C(8)—C(7)	110.9 (2)	C(16)—C(17)—C(13)	103.0 (2)
C(14)—C(8)—C(9)	108.7 (2)	C(18)—C(17)—C(13)	116.5 (2)
C(23)—C(8)—C(7)	108.1 (2)	C(18)—C(17)—C(16)	110.4 (2)
C(23)—C(8)—C(9)	112.9 (2)	C(19)—C(18)—C(17)	125.4 (3)
C(23)—C(8)—C(14)	105.9 (2)	C(21)—C(18)—C(17)	129.4 (2)
C(10)—C(9)—C(8)	115.2 (2)	C(21)—C(18)—C(19)	105.2 (3)
C(11)—C(9)—C(8)	111.9 (2)	C(18)—C(19)—O(4)	111.2 (3)
C(11)—C(9)—C(10)	114.5 (2)	C(21)—C(20)—O(4)	110.6 (4)
C(5)—C(10)—C(1)	107.4 (2)	C(20)—C(21)—C(18)	107.0 (4)
C(6)—C(5)—C(10)—C(22)	-64.8 (3)	C(8)—C(14)—C(13)—C(24)	85.4 (3)
C(5)—C(6)—C(7)—O(2)	-63.4 (3)	C(14)—C(13)—C(17)—C(18)	77.8 (2)
C(13)—C(14)—C(8)—C(23)	107.5 (2)	C(13)—C(17)—C(16)—O(3)	165.3 (2)

	C...O/O...O	H...O	C—H...O/ O—H...O	Symmetry operation
O(2)—H(2)...O(3)	2.977 (3)	2.00 (5)	177 (2)	$1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
C(19)—H(19)...O(1')	3.227 (4)	2.83 (6)	101 (3)	$x, 1 + y, z$
C(20)—H(20)...O(1'')	3.281 (4)	2.53 (6)	137 (3)	$-1 + x, 1 + y, z$
C(23)—H(232)...O(2')	3.193 (3)	2.72 (5)	111 (2)	$-1 + x, y, z$

tance C(1)—C(2), 1.317 (4) \AA , is shorter compared to the other three C=C distances [C(14)—C(15), C(18)—C(19) and C(20)—C(21)] in the molecule, with an average value of 1.344 (4) \AA .

Fig. 2 shows the molecular stacking in the unit cell. Along with O—H...O interactions, intermolecular C—H...O interactions (Taylor & Kennard, 1982; Das, Sinha, Narkhede & Manisekharanan, 1990) are observed (Table 2).

References

- DAS, K., SINHA, U. C., NARKHEDE, D. D. & MANISEKHARANAN, T. (1990). *Acta Cryst.* **C46**, 1888–1890.
 GAIKWAD, B. R., MAYELVAGANAN, T., VYAS, B. A. & BHAT, S. V. (1990). *Phytochemistry*, **29**, 3963–3965.

- KRAUS, W., CRAMER, R. & SAWITZKI, G. (1981). *Phytochemistry*, **20**, 117–120.
- MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- PILLAI, N. R. & SANTHAKUMARI, G. (1981). *Planta Med.* **43**(1), 59–63.
- PILLAI, N. R. & SANTHAKUMARI, G. (1984). *Planta Med.* **50**(2), 143–146.
- SCHMUTTERER, H. & ASCHER, K. R. S. (1983). In *Proceedings of the 2nd International Neem Conference*, Ravischhalzausen, Germany. Eschborn: Ot. Gesellschaft für Technologie Zusammenarbeit.
- SCHMUTTERER, H., ASCHER, K. R. S. & REMBOLD, H. (1980). In *Proceedings of the 1st International Neem Conference*, Rottach Egern, Germany. Eschborn: German Agency for Technical Cooperation.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SIDDIQUI, S., SIDDIQUI, B. S., FAIZI, S. & MAHMOOD, T. (1988). *J. Nat. Prod.* **51**, 30–43.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

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Structure of 2-Aminodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphpine-2-thione–Di-*n*-butylamine Adduct

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Abstract. $C_{29}H_{33}N_2O_2PS$, $M_r = 492.6$, triclinic, $P\bar{1}$, $a = 8.8737(6)$, $b = 12.6312(8)$, $c = 13.8424(8)$ Å, $\alpha = 111.797(6)^\circ$, $\beta = 104.103(5)^\circ$, $\gamma = 97.005(5)^\circ$, $V = 1357.9$ Å³, $Z = 2$, $D_x = 1.20$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 17.9$ cm⁻¹, $F(000) = 524$, $T = 295$ K, $R = 0.065$ for 4778 observed reflections. The seven-membered phosphpine ring is in a boat conformation. The bond length, P=S, is 1.924(2) Å. The naphthalene rings are planar. The crystal structure is stabilized by an N—H \cdots N intermolecular hydrogen bond N(24) \cdots N(25) with N \cdots N distance and N—H \cdots N angle 2.72(2) Å and 166.5(2)°, respectively.

Introduction. The chemistry of organophosphorus compounds has received tremendous attention during the past two decades because of its vital role in both life-sustaining and life-destroying activities (Corbridge, 1975; Garcia-Blanco & Perales, 1972). The title compound belongs to the category of life-destroying substances *viz.* insecticides, bactericides, flame retardants, *etc.* (Ismail, 1975). The organophosphates form a wide spectrum of insecticides and pesticides effective against aphids, mites, lepidoptera, beetles, leaf-hoppers and thrips on fruits, vegetables and crops, and for this reason its X-ray structure is of great interest to our continuing investigations.

Experimental. Transparent needle-shaped crystals were obtained by slow evaporation from methanol. Crystal, 0.53 \times 0.23 \times 0.08 mm, used for all measurements. Accurate cell parameters obtained from least-squares refinement using 2θ values of 25 medium-angle reflections ($35 < \theta < 45^\circ$). Intensity data collected using $\omega/2\theta$ scan technique on Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Intensities of two standard reflections monitored periodically during data collection, no significant variation. Intensities of reflections $2 < \theta < 75^\circ$ measured (h : -10 – 10 , k : -14 – 14 , l : 0 – 14). 5385 independent reflections measured, 4778 reflections had $I > 3\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects, no absorption correction was applied. The structure was solved by direct methods using the program *SHELXS86* (Sheldrick, 1986). All the H atoms except those attached to N atoms and methyl group atoms located on a difference density map. H atoms attached to N atoms and methyl groups fixed geometrically and checked in the difference map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined (on F) by full-matrix least-squares methods. Final $R = 0.065$ and $wR = 0.075$ for 4778 observed reflections, $w = K/(\sigma^2|F_o| + m|F_o|^2)$ ($K = 2.3900$, $m = 0.000469$).